PLATINUM SILVER ALLOYS

By

JOHN FAIRFIELD THOMPSON, B. S.

Dissertation

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University

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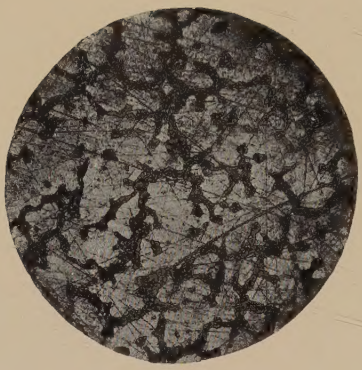
1906



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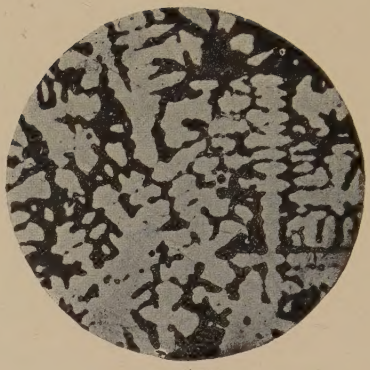

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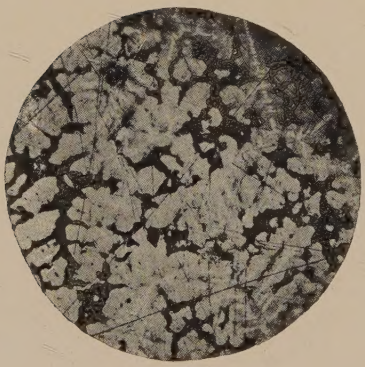

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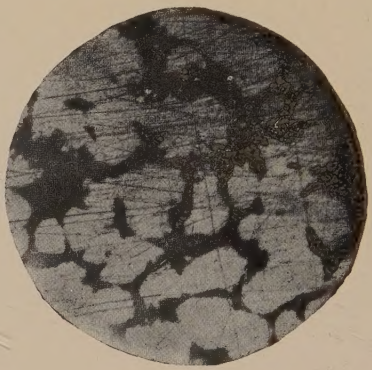

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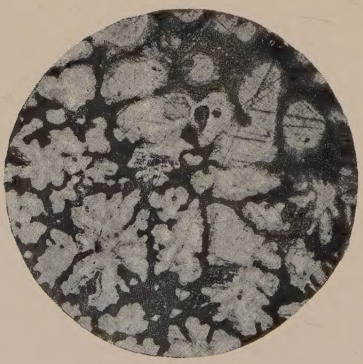

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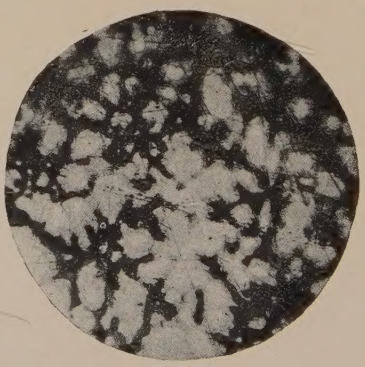

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LUDO BAT.
BIBL.

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INTRODUCTION

The lack of agreement among the statements of various authors as to the quantitative effect of nitric acid on platinum silver alloys led to the conclusion that further investigation on these lines would be of value, as showing more conclusively the strength or weakness of the several analytical methods based on a supposed complete solubility of one or more of these alloys. Beside this, it was desired to determine certain of the physical properties of these alloys on samples of proved composition, purity and homogeneity.

ACKNOWLEDGEMENT

The following investigation was undertaken at the suggestion of Professor Edmund H. Miller, and was carried out under his direction. I wish here to express my thanks for the assistance rendered, and my appreciation of his interest and encouragement throughout the entire course of the work.

J. F. T.

Quantitative Laboratory,
Havemeyer Hall, Columbia University,
June 1, 1906.

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HISTORICAL.

The solubility of platinum, when alloyed with silver in nitric acid, may be considered one of the historical facts in the history of the metal, as its announcement by the Graf von Sickingen (1) in 1782, came only forty-six years after the discovery of the element platinum, thus placing it among the earliest known chemical properties. The reasons for and quantitive relations of this solubility have, however, remained unexplained up to the present day, in spite of the numerous attempts on the part of various experimenters. The results of these authors have been conflicting in the extreme, and not only have the later investigators failed to confirm the earlier, but their results in themselves offer no explanation as to the cause of the anomalies. Thus, Clemens Winkler (2), working with alloys containing percentages of platinum varying from 1% to 10%, found that the strength of acid used was of small importance, while the weight of residue left, assumed by him to be platinum, was on the average about 66% of the weight of the original alloy. This percentage varied somewhat irregularly with the strength of acid and percentage of platinum in the alloy, and, in general, decreased with the platinum content of the alloy. John Spiller (3), on the other hand, investigating alloys of the same range of platinum content, found acid of 1.42 specific gravity to be the best solvent, but records that, even under the most favorable conditions, only 0.75 to 1.25% of the platinum could be dissolved along with the silver. H. Rose (4) found that, at the most, 10% went into solution with the silver. N. W. Perry(5), in a description of an assay method, states that after removing the base metal by cupellation, the platinum could be dissolved completely along with the silver, provided the platinum were alloyed with at least twelve times its weight of silver. E. H. Miller (6), in a comparison of the various wet and assay methods for the determination of platinum, repeated Perry's work and found that, even with a platinum silver ratio of twenty-seven to one, some platinum remained undissolved. The results in this case were, however, complicated by the presence of iridium and gold in the material experimented on. Later, von den Ropp (7), in a series of experiments on alloys containing up to 30% of platinum, found that alloys containing not more than 23% of platinum could be brought completely into solution by treating them with nitric acid, washing the residue free from nitric acid with water and then treating with hydrochloric acid. Beside this new and positive fact

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(1). Muspratt. 4th Ed., 7, p. 255.
(2). Zeit. fur Analyt. Chem., 1874, p. 368.
(3). Proceed. of the Chemical Soc., 13, 118, 1897.
(4). Rose, Hand. der Analyt. Chem., 6th, Ed. 2, 226.
(5). Engineering and Mining Jour., January, 1879.
(6). School of Mines Quarterly, 17, 26, 1895.
(7). Berlin Dissertation. 1900.

brought out by von den Ropp's work, he also investigated to some extent the black residue, left on treating the alloy with nitric acid, and tried the solvent effects of hydrochloric acid, sulphurous acid and ammonia in the order named, the treatment with each reagent being followed with a complete washing of the residue with water, the solutions and wash waters being kept separate. In this way von den Ropp obtained a series of solutions or colloidal solutions. The cause of the solution of parts of the residue in this way, or the composition of the parts dissolved were, however, not investigated. Finally Krug (1), in an investigation of the alloys of platinum and copper, found that the residue left on dissolving the alloys in nitric acid, and which he, as well as Winkler and von den Ropp, found to be explosive when heated with organic materials, *i.e.* filter paper, consisted of a nitrate. Krug explains the solubility found by von den Ropp (see above), as being merely a reaction of the hydrochloric acid used against this compound giving chlorine which dissolved the platinum. He also advanced the idea that the solutions obtained by von den Ropp with various reagents were simply forms of colloidal platinum. This latter idea will be discussed later in connection with some further solubility experiments. Beside these investigations of the solubilities of the binary alloys of platinum, several papers have been published dealing with experiments on the parting of ternary and even quaternary alloys containing platinum and silver. The results have in most cases been unsatisfactory, as the problem, which in the case of binary alloys, presented wide inconsistancies in similar work done by different investigators, has in the case of ternary and quaternary alloys become so complicated that it is impossible to decide what variable is responsible for any given set of results. The papers dealing with this phase of the subject will, therefore, not be reviewed in full, but will only be referred to when their results have some direct connection either with our experimental results or conclusions. In a footnote, reference will be found to some of the more important or recent. (2)

As may be seen from the foregoing review, neither the primary fact of why platinum dissolves when alloyed with silver, or the secondary facts as to the quantitative relations of this solution have ever been firmly established. Chemical investigation alone would be enough to settle the latter. It is difficult to see, however, how strictly chemical methods could ever solve the first problem or give the basis on which the results of solution tests could be satisfactorily interpreted. The following investigation was therefore started with the idea of investigating the physical properties of the platinum silver alloys and using the results so obtained in the interpretation

(1). Leipzig Dissertation. 1903.

(2) Carmichael. J. Society of Chemical Ind. 22; 1324, 1903.
Sharwood. J. Society Chemical Ind. 23; 412, 1904.
Richards, Analyst. 27; 265, 1902.
Neveu Ann. Chim. anal. appl. 8; 161.
Hollard and Butiaux, Ann. Chim. anal. appl. 9; 287.

of a series of solubility tests run in comparison with those of previous investigators.

The physica properties chosen for investigation were the melting points and cooling curves, microstructure, specific gravity and electrical conductivity of the different alloys. These, it was felt, would give a sufficiently wide range of properties, so that reliance could be placed on a confirmation of the results of one series by those of another. A careful survey of the literature was made before beginning this study, with very little result. In this connection the assistance obtained from the excellent bibliographies of Howe (1) and Sack (2) should be acknowledged. On cooling curves the only quantitative data which could be found was that given by a partial curve published by Heycock and Neville (3). These authors investigated alloys containing up to 2 atomic per cent (4) of platinum (3.55% by weight) and found that the freezing point curve rose sharply away from the freezing point of silver, the alloy containing 2 atomic per cent of platinum freezing at 990 degrees Centigrade. Matthiesen (5) in an account of some experiments on certain platinum silver alloys refers to the 33% alloy being at a critical point in electrical resistance. Beyond these references all data that could be found was either inapplicable to the present work or too vague as to percentages of platinum, etc., to be of any use.

EXPERIMENTAL

The first step was the purification of the materials used and the preparation of alloys of known composition and proved homogeniety, the last two points being questions which had been neglected by previous investigators.

Purification of Materials.

The platinum used was a supposedly C. P. foil from a foreign maker, but was shown by qualitative analysis, using the method of Mylius and Dietz (6), to contain iridium. It was, therefore, freed from this by the following purification method (7). This con-

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(1) Bibliography of the Metals of the Platinum Group. Smithsonian Misc. Collections. Vol. 38; No. 1084.
(2) Bibliographie der Metallegierung. Zeit. für Anor. Chem. 35,249; 1903.
(3) Phil. Trans. Roy. Soc. 189; A. 25, 1897.
(4) Atomic per cent may be calculated as follows, for any series of binary alloys A—B:

$$\text{Atomic \% A} = 100 \frac{\dfrac{\text{weight A}}{\text{atomic weight A}}}{\dfrac{\text{weight A}}{\text{atomic weight A}} + \dfrac{\text{weight B}}{\text{atomic weight B}}}$$

Weight A and B being taken as parts in 100.

Grube. Z. Anor. Chem. 44; 122, 1905.
(5) J. Chemical Soc. Lond. 20; 201, 1867.
(6) Berichte, 1898, 3137.
(7) Encyclopedia Britt. Ninth Edit. 19; 201.

sisted in dissolving the impure platinum in aqua regia and freeing from nitric acid by repeated evaporations with hydrochloric acid. This hydrochloric acid solution, containing both of the elements in their highest state of oxidation, was then taken to dryness and heated on an electric hot plate for several hours at a temperature of 125 degrees Centigrade. It was then taken up with hydrochloric acid and water and precipitated by the addition of ammonium chloride and alcohol. The iridium, which had been reduced by the heating to a lower chloride, not being precipitated by the ammonium chloride, passed into the filtrate along with some of the platinum, also reduced. The platinum ammonium chloride was then dried and tested for purity by spreading it out on a glazed paper and examining portions selected from different parts thoroughly under a microscope (80 diameters). In no case, although eight separate portions were examined from each lot, could any salt be detected except the yellow crystals of platinum ammonium chloride. This salt was then converted to metallic platinum by ignition and washed successively with hydrochloric acid, water, nitric acid and water. The sponge so obtained was either used as such or melted with the oxy-hydrogen blow-pipe and rolled out into foil.

The silver was furnished by a reliable maker as being 999 fine or better, and was used without further purification. As will be shown later, the thermal analysis enabled us to make a check on the purity of the silver by means of a determination of its melting point.

Preparation of Alloys.

To be used for a preliminary survey of the field five alloys, weighing ten grams each, were made, containing approximately 10,20, 30,40, and 50% of platinum. The method of preparation was the same throughout, except that the 40 and 50 % alloys were made from the platinum sponge on account of the greater ease of alloying compared with the foil from which the others were made. In all cases, the silver was first melted in a No. 1 French clay crucible in a small Fletcher furnace. After it was thoroughly melted, the silver was added piece by piece, if used as foil, or wrapped in an ashless filter paper, when the sponge was employed. Heating was continued for about five minutes, when the crucible was withdrawn from the furnace and shaken violently until the melt solidified. It was then replaced, and this treatment, melting, holding melted for 2-3 minutes and then removing and shaking until the button solidified, repeated several times. The crucible was then removed from the furnace and the button allowed to solidify and removed from the crucible. It was then replaced in the crucible in an inverted position and the previous treatment repeated, so that any pieces of platinum which might have sunk to the bottom of the button and so escaped, more or less, the effect of the several shakings, would come more intimately in contact with the melt. After several such heatings the button was allowed to cool and was cut in half vertically. One of the faces so exposed was then polished and

examined with a metallographic microscope for any pieces of unalloyed platinum. If any such were found, the alloy was remelted and the previous treatment repeated until no platinum could be found unalloyed on careful microscopic examination. In cutting the alloys for microscopic examination, considerable difference in their hardness was noted, which will be discussed later in connection with their other physical properties. Before starting the preparation of the alloys, it was feared that the furnace used would not give sufficient heat to melt the alloys of higher platinum content. This fear was, however, without foundation, for using a false top, so that a higher rate of combustion could be used and also a supplementary blast-lamp of the Waller type, blowing in at the same tuyere hole as the regular blast, it was found that temperatures of 1,450 degrees Centigrade could be reached in the crucible.

Thermal Analysis.

The freezing points and cooling curves of the alloys were next taken in the Fletcher furnace, the No. 1 French clay crucible holding the alloy, being surrounded by a larger crucible to decrease the rate of cooling. The method used was that of direct observation, using a Siemens and Halske galvanometer and a platinum-platinum 10 % iridum thermocouple. The wires for this couple were made with great care in order to insure perfect homogeneity. In fact the platinum iridium was melted and shotted in water four times before the final ingot was cast. The wires were next thoroughly annealed by means of electrical "glowing" to remove any strains from the wire drawing and were then investigated and found to be thermoelectrically homogeneous. This was done by taking each wire and connecting one end to each of the terminals of the galvanometer by means of two copper wires, the ends of the platinum or platinum alloy wire being contained in an ordinary cold junction bottle. By heating successive places on the wire, it could be shown that the wire itself was homogeneous throughout, or at least that there were no sudden variations in composition. That the wires were not of progressively changing composition was shown by making each end of the wire successively the hot junction and comparing with a second couple. The maximum error found in this way amounted to 2 degrees Centigrade. This precaution of testing for thermoelectric homogeneity is essential in case it is not desired to make use of more than one junction in a series of determinations of a single point and especially in a Fletcher furnace, where the length of couple heated can not be conveniently varied to suit the convenience of the operator. The wires of the couple having been annealed and shown to be homogeneous, the couple was next standardized, against the boiling point of pure sulphur, using a Barus boiling point tube, and against the freezing point of Kahlbaum's copper. The sulphur used was in the form of crystals from carbon disulphide and was boiled thoroughly to free from any carbon disulphide, either of crystallization or mechanically held. Its boiling point was taken as 444

degrees Centigrade (1.) The freezing point of the copper was taken as 1,084 (2.) degrees Centigrade and the determinations were made under a layer of charcoal, the copper being melted under this layer, held melted for some time and also polled with a stick to insure complete reduction. From these points the curve of the couple was calculated, using Holman's logarithmic formula (3). As a check on the accuracy of this curve, the melting point of Kahlbaum's antimony was next determined, and in all cases fell within a limit of error of 3 degrees Centigrade from the temperature of 630 degrees Centigrade which was taken as the true melting point (4). A further check on the accuracy of the standardizing was obtained by the determination of the freezing point of silver, which was determined in a graphite crucible under a layer of charcoal. This also in every case fell within the 3-degree limit and formed a very good check on the purity of the silver used in the preparation of the alloys. The melting point of pure silver free from oxygen was taken as 961 degrees Centigrade (2). In taking the melting points and cooling curves of the alloys themselves it was not possible to use a charcoal cover as the disturbing influence of oxygen was preferable to any risk of the platinum forming a carbide or taking carbon into solution. It is probable that this influence was of importance only in the alloys of lower platinum content, as with the higher alloys no noticeable spirting took place. Several experimental difficulties arose in these freezing point and cooling curve determinations, due largely to the use of such small amounts of alloy as to make the heat evolutions at any one temperature very small. In all cases the couple cover was clamped in place so that the end of the couple would come as near as possible to the center of the melt.

ELECTRICAL RESISTANCE, SPECIFIC GRAVITY AND DUCTILITY

After the thermal analysis had been finished, the alloys were remelted in crucibles of such a shape that the resulting buttons were in the form of cylinders of approximately 9 mm. diameter. A section was cut from the bottom of each button and reserved for microscopic examination while the remainder of the button was rolled out into tape. The rolling out of the alloys was kindly done for me by Mr. Cohn of the platinum-refining firm of Belais & Cohn of New York City. From this tape a piece of uniform cross-section was cut out which was thoroughly annealed and used for the measurement of the electrical resistance. This measurement was done for me on a Wolff bridge, by Mr. A. H. Nelson, of the Department of Physics, to whom I wish to express my thanks.

(1.) LeChatelier and Boudouard, High Temperature Measurements, 2nd Eng. Ed., 296.
(2.) Holborn and Day, Am. J. Sci., 11, 145, 1901 and 8, 165, 1899.
(3.) Holman, Proc. Am. Acad. 31, 234.
(4.) Day and Allen, Physical Review, Sept., 1904.

ELECTRICAL RESISTANCE
EXPRESSED IN OHMS PER SQUARE MILLIMETER PER METER
ALLOY.

0 Platinum 100 Silver	.....	0.0217
10.39 Platinum	.....	0.0918
20.59 "	.....	0.1814
31.46 "	.....	0.2914
37.89 "	.....	0.3110
57.05 "	.....not determined	

The alloys were then cut into small pieces, by means of a large pair of tin shears for further investigation. In this connection the very interesting qualitative fact may be noticed of the very marked change in ductility and in actual hardness which accompanied the increasing platinum content. This had already been noticed when cutting the alloys up for the different microscopic examinations and the same observations were repeated when the alloys were rolled. Thus the pure silver cut and rolled in manner to be expected from its well-known soft and ductile nature. That is, the hack saw was not appreciably dulled by cutting a button and, in rolling several passes, could be made each time before the button had to be annealed. The 10 and 20% buttons were very much like it in both of these properties. With the increase of the platinum content up to 30%, however, a marked change was noted in the behavior of the buttons. In cutting, the buttons were much harder and this hardness increased rapidly with the increasing platinum content. Thus, while the 31% button cut with more difficulty than the lower ones, but was still comparatively soft, the 57% alloy was, on the other hand, so hard that several saws were broken each time a button had to be cut. This property was still more marked in the case of the rolling, and was shown by the increasing frequency with which the alloys had to be annealed in order to get them to go through the rolls without cracking. The limit of this was reached with the 57% alloy, which would stand almost no reduction and cracked so badly on the first pass that further rolling and, therefore, the measurement of its electrical resistance, had to be abandoned. Since the object of the investigation was to study simply those properties which would tend to throw some light on the chemical behavior, the question of changes in hardness was followed no further and no attempt was made to check these very rough qualitative results by means of sclerometer measurements.

The alloys having been cut up into small pieces, their specific gravity was measured, using a weighing bottle, as compared to that of water at 4 degrees Cent., with the following results:

Pure Silver	10.61
10.39	11.17
20.59	11.80
31.46	12.57
37.89	13.19
57.05	14.25

ANALYSIS

In order that the results on the various alloys might be referred to alloys of known composition, the alloys were analyzed by means of the standard parting with sulphuric acid. From the table of results, given below, the necessity of this step is plainly shown and gives some explanation as to the cause of the anomalous results of some previous investigators, who in no case had any further knowledge of the composition of their alloys than that gained from the proportions used in making them up. As in making our alloys the quantities of the metals were weighed exactly for making alloys of 10, 20, 30, 40 and 50% of platinum, the magnitude of the error even when working carefully in crucibles may be observed, and show that the composition of the alloys made on charcoal befo e a blow-pipe can only be a matter of conjecture, no matter however carefully the materials may have been weighed out. As carried out, the parting differed somewhat in detail from that as generally described. In fact the methods as given in most descriptions of the process could not fail to give inaccurate results. One description provides for parting 300 milligrams of the alloy for 15 minutes over a Bunsen burner in a parting flask with 10 cc. of pure concentrated sulphuric acid. The acid was then allowed to cool and decanted into a beaker containing distilled water. The residue was treated as before with 5 cc. of strong sulphuric acid and decanted into the same beaker. Washed till free from acid, adding the washings to the silver sulphate solution. The platinum is then transferred to a small crucible by inverting, dried in an air bath and weighed. By this means the author, working on an alloy containing over 33% of platinum, obtained results differing only by one-tenth% on four separate determinations, and states that the platinum was tested for silver, but was found to contain only a minute trace. He further states that the silver may be estimated in the filtrate by the thiocyanate method, or, as in his work, by difference.

In attempting to follow out this method in the analysis of my alloys, it was found that, even with closely agreeing duplicates, entirely erroneous results were obtained, for the following reasons: 1st. In decanting the sulphuric acid solution from the residue platinum passed over with the solution. This platinum was in either a very finely divided or colloidal state, giving a dark color to the solution. The state of division was so fine, that not even by allowing the beaker containing the decanted filtrate to stand

on a piece of white paper could any particles be seen as such. That they were present, however, is shown by the fact of their separating, if the solution was allowed to stand over night. And further, the fact that this separation on standing was due to particles already contained in the solution, and not formed by some unnoticed reaction during standing, was shown by taking two portions of the same alloy and parting in the same way with sulphuric acid. One of these solutions was decanted and allowed to stand over night, and in the morning a fine black precipitate was found on the bottom of the containing beaker. The second solution was diluted and filtered, when a black precipitate was found on the filter paper, and the filtrate on standing threw down no further precipitate. 2nd. The platinum residue left, always contained some silver. This was less in amount with the lower platinum alloys, but was always a weighable quantity, and in the higher alloys became of very considerable importance. The use of the thiocyanate method for determining the silver in the filtrate was tried, but was not successful, in the presence of the large amounts of sulphuric acid from the solution of the alloy. By precipitating the silver from this acid solution with aluminium foil, dissolving in nitric acid and titrating, better results could be obtained, but the duplicates were not satisfactory. The method finally adopted was as follows: 300 milligrams of the alloy were taken and heated for 15 minutes in a beaker with 10 cc. of concentrated sulphuric acid on an asbestos pad over a Bunsen burner. This solution was then decanted into a beaker and the alloy broken up by poking the pieces with a stirring rod and then re-treated for 15 minutes with 5 cc. more of concentrated sulphuric acid. The solutions were then combined, diluted, filtered through an ashless paper, and washed till entirely free from silver salts. The residue on the paper was then ignited in a porcelain crucible and weighed. This residue was then dissolved in aqua regia and by several treatments with nitric acid, followed by taking the solution gently down almost to dryness most of the free acid was removed, and the free acid that remained was nitric and not hydrochloric. The solution was then diluted somewhat, and the silver precipitated by the addition of common salt in the usual way. The precipitate obtained in this manner was of a reddish yellow color, apparently due to admixed silver chlorplatinate. This precipitate was filtered and washed free from chlorides. It was then dissolved through the paper with dilute ammonia and reprecipitated in the filtrate with nitric acid and a drop or two of hydrochloric acid. Filtered and weighed in the regular way. It was found that this solution of the impure silver chloride and reprecipitation gave a perfectly white precipitate, while the platinum passed into the filtrate. The strong sulphuric acid solution containing the silver was treated in one of two ways: 1. By diluting to about 900 cc. partly neutralizing and precipitating the silver as sulphide at a temperature of about 90 degrees. Filtering, dissolving the sulphide in nitric acid and reprecipitating the silver

as chloride, in which form it was weighed. 2. The effect of precipitating the silver as chloride direct in the sulphuric acid solution with common salt, after partly neutralizing with ammonia was tried, with practically the same results as obtained by the first and longer method of procedure. In either case the precipitated silver chloride was washed till the washings gave no test with silver nitrate, while the filtrates were all tested with hydrogen sulphide to be sure that the summations obtained were not due to any balancing of error. The sulphuric acid used in the parting was tested and found to contain no nitric acid. In some cases, however, unweighable traces of platinum could be found in the filtrate, by means of an examination with a microscope on the concentrated filtrate when tested with ammonium chloride. This was neglected in our work, and no attempt was made to separate it from the silver, which it contaminated, as the amount present was very small. In this connection, a paper by Delépine 1, lately published, is of interest as showing the amounts of platinum that may be dissolved by concentrated sulphuric acid on long treatment. In these parting experiments, however, the time of action is so much reduced that the solvent action on the platinum is negligible. The results follow:

% Pt. supposed.....	10.00	20.00	30.00	40.00	50.00
% Pt. actual.....	10.39	20.59	31.46	37.89(2)	57.05
% Ag. retained by Pt.	tr.	.59	.98	2.24	2.70
% Ag. in filtrate.....	89.54	78.62	67.51	59.81	40.26
Summation.....	99.93	99.80	99.95	99.94	100.01

As may be seen from the previous tables, these results have been used to correct the supposed platinum percentages on the alloys.

Microstructure.

The specimens which had been reserved for the microscopic examination were next prepared for examination and photographing by polishing them successively on rough and smooth Armouremery paper, and on 0, 00, 000, and 0000 Hubert French emery paper. The polishing was finally finished on baize on a rough board, using carefully washed jewelers' rouge. Etching was done with 1.1 specific gravity nitric acid. For examining and photographing the alloys, a Reichert microscope was used in connection with a Bausch and Lomb photomicrographic camera, using a Welsbach illumination and an inside illuminator. All photographs were taken at a magnification of 100 diameters.

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1. Comptes Rendus, 142, 631, 1906, alstr. J. S. C. I, 25, 314, 1906

2. The very low platinum content of this alloy can only be explained by the accidental loss of platinum during the preparation, as duplicates show that the figure for platinum as given above is correct.

Results of Thermal Analysis and Microscopic Examination.

Heycock and Neville (1), in their investigation of a limited portion of the platinum silver cooling curve, found that with increasing platinum content, up to the limit of their investigation, the melting point rose regularly, their alloy of maximum platinum content (3.55%) having a melting point of 990 degrees Centigrade. In my own experiments the alloy containing 10.39% of platinum was heated to 1,200 degrees Centigrade, and the cooling curve taken from that point. Two evolutions of heat were noticed, the first 1,045-1,050 degrees and the second and much larger at 1,000 degrees. Owing to the conditions of radiation from the furnace there was always a slight drop of temperature throughout, when operating with alloys as small as ten grams, and it was not possible to determine whether solidification was complete at 1,000 or not. The alloy, when examined under the microscope, was found to consist of crystals set in a ground mass, which was not composite, or at least, which could not be resolved by the highest power available. This is not, however, a positive proof that the ground mass had not frozen out as a eutectic and afterward become simple by segregation, a fact of common occurrance when the eutectic is small in amount. The 20.59% alloy was heated to 1,100 degrees Centigrade, and on cooling evolved heat strongly at 1,085 degrees Centigrade, and possibly again at 995, although the indications at the latter point were hardly beyond the experimental error. The microstructure at this point showed large, white dendrites also set in a non-composite ground mass. The 31.46% alloy was heated to 1,300 Centigrade and a cooling curve taken down to 970 degrees Centigrade. Marked evolutions of heat took place in the range between 1,170 and 1,100 Centigrade. They were, however, very irregular and were different in their exact location in different trials. The examination of the alloys under the microscope showed well-defined crystals of a grayish color set in a dark ground mass. These gray crystals had each a perfectly white silvery core or spine, which offers a clue to the irregularities of the cooling curves. This is, that the rate of cooling was so rapid that the alloy passing through transformation points did not have time to come to equilibrium, and this result is shown both by the microstructure and by the cooling curves. In the cooling curves this is shown by the heat liberations at any one temperature being very small and also confused, owing to heat liberations from two separate causes taking place at the same time in different parts of the button. The most regular of the curves show, however, a consistent evolution of heat at 1,160 degrees Centigrade, and this is taken as probably correct. There are also weak indications at about 1,230° Centigrade. In the microphotographs this is shown by the white core in the centre of the crystals, which disappears when the alloy is remelted and allowed

(1.) Loc. cit.

to solidify and cool very slowly in a gas furnace. (See photomicrographs). The 37.89% platinum alloy, while showing much the same characteristics in its microstructure as the 31.46% alloy, i.e., gray crystals with white centres set in a dark ground mass, gives much sharper heat evolutions during its cooling. These are at 1,240 Centigrade, not very strong but consistent for all curves, and a second at 1,170 Centigrade, which is strongly marked in all curves, and is the most marked evolution for this particular alloy. Unfortunately, the curve was only once continued below 1,000 degrees, and in this case was too irregular to be of any value. The 57.05 alloy was heated to over 1,400 degrees Centigrade, and on cooling gave evolutions of heat at 1,240, 1,180 and 1,090 degrees Centigrade. In microstructure it appeared very much like the 37% alloy.

The investigation of the solubility of the alloys in nitric acid was next proceeded with according to the following scheme:

SOLUBILITY TESTS IN 1.1 NITRIC ACID

Method of Procedure.

C. P. nitric acid was diluted with distilled water and after cooling the concentration was adjusted with water to 1.1 specific gravity to within the limit of accuracy of a delicate hydrometer. Three hundred milligrams of each of the alloys, cut into small pieces (1mm.—2mm.—2mm.) were next weighed out into No. 2 beakers and 25 c.cm. of the 1.1 acid added to each. These were placed on an electric hot plate and heated rapidly to 70, or 80 degrees Centigrade and kept at that temperature for an hour, the temperature being observed by means of thermometers. At the end of 20 minutes the alloys were broken up by means of the thermometers, so as to prevent as far as possible the effect of any mechanical coating. After an hour the solutions were removed from the stove and allowed to stand for 1¼ hours after diluting to about 75 c.cm. The solutions were all somewhat colored, the 20 and 31% ones especially, the order of decreasing intensity of color being 20, 31, 37, 57 and 10. Of these the 20 was almost black and was opaque, the remainder rapidly shaded down in color to the 10, which was almost colorless. The solutions were then filtered through 7 cm. ashless filter papers, when it was found that the filtrates bore the same color relation as the original solutions. On attempting to wash the precipitates with distilled water, they washed through the paper readily and acted in the manner common to all colloidal precipitates. The filtrates and wash solutions were therefore combined and the precipitates salted out with sodium nitrate free from chloride. After standing they were filtered through the same filter paper as before, and on washing with 1 % nitric acid (*i.e.* 1 cc. of 1.42 acid in 100 of water) it was found that they could be washed free from silver without loss from the formation of any colloidal precipitate. After ignition in porcelain crucibles

they were weighed, dissolved in aqua regia and the contained silver determined as in the case of the analysis of the alloys. During the ignition, slight explosions due to the precipitate reacting with the filter paper could always be noticed. The results follow, the one given for the 31.46 % alloy being determined on the alloy in the rapidly cooled state.

% Pt. in Alloy	10.39	20.59	31.46	37.89	57.05
% Residue	3.86	8.58	36.59	49.13	65.16
% Ag. in "	0.27	1.81	12.09	13.64	12.19
% Pt. in "	3.59	6.77	24.50	35.49	52.97

Evidently, from the foregoing any ratio of platinum and silver which will allow of complete solution of both in nitric acid must lie within considerably closer ranges than those investigated above. A further series of alloys was therefore made in order to test further for this point. These alloys were made in the same way as the previous set and were examined microscopically for homogeneity. Parting tests were conducted as before with 1.1 nitric acid except that the silver content of the residues was not determined, as the object was to find a completely soluble ratio, or failing that the most nearly soluble ratio to test the process as a means for analytical separation. Since Miller's (1) work had shown that with a platinum content of 4 % some residue was left, the alloys below that point were investigated thoroughly. Besides these alloys were made at ratios selected by means of the cooling curves and certain alloys were selected arbitrarily in order that the solubility results might not have to be interpolated except over very narrow ranges. The results follow; those for the 31.46 % alloy in this case being on the very slowly cooled alloy.

% Pt in Alloy	0.50	1.00	2.00	3.00	4.00	5.00	
% Residue.	0.42	0.85	1.74	2.19	2.98	3.56	
% Pt in Alloy	13.00	14.00	15.00	16.00	18.00	25.00	31.46
% Residue	3.33*	4.26	4.32	4.55*	4.54*	16.62	38.58

*average of two figures.

In these tests as well as those of the previous series the formation of colloidal platinum was very marked, especially with the alloys near to 20% of platinum. When this had been completely removed by means of ammonium nitrate and heat, the solutions were still colored but this coloration was very slight and no further separation took place in solutions containing considerable ammonium nitrate and nitric acid, even on standing several days.

The foregoing results show clearly the impossibility of separating platinum from gold, iridium, etc., by one parting with nitric acid

(1.) Loc. cit.

after alloying with silver and also the fallacy of assay methods such as Perry's (1) based on this supposed separation. As may be seen from the above tables the ratio of residue to platinum in the alloy is lowest in the alloys containing 13 to 18% of platinum and is on the average about 30% of the weight of platinum present. Repeated alloying with silver at these ratios and solution in nitric acid would probably effect complete solution of the platinum. Whether this would effect a complete separation from iridium at the same time, or whether some of the iridium would go into solution with the platinum can only be settled by direct experiment. Alloying with higher percentages of silver would be of no value as in these cases a residue is left which amounts to about 85% of the weight of platinum in the alloy, while alloying with less silver gives an alloy which on parting gives a residue which weighs more than the platinum contained in the alloy.

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1. loc. cit.

CONCLUSIONS

1. The separation of platinum from gold, iridium, etc., in one operation by means of alloying with silver and parting with nitric acid is impossible.

2. Analytical results on platinum silver alloys, based on parting with concentrated sulphuric acid, are incorrect for alloys containing 20% or more of platinum, unless correction is made for the undissolved silver remaining with the platinum.

BIOGRAPHICAL

John Fairfield Thompson entered the School of Chemistry of Columbia University in September, 1899, and was graduated in 1903, with the degree of Bachelor of Science. From July, 1903, until June, 1906, he filled the position of Assistant in Metallurgy, in the School of Mines of Columbia University, and at the same time pursued graduate work for the degree of Doctor of Philosophy, under the Faculty of Pure Science.